# REPORT DOCUMENTATION PAGE

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DISTRIBUTION STATEMENT A. Approved for public release; distribution is unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

It is imperative for pyrotechnic testing facilities to operate with relatively low concentrations of any potentially hazardous chemical contamination. New regulations are already impacting the operation of these facilities and accordingly are driving toward the elimination of several currently utilized components (e.g., perchlorates and chromates) within pyrotechnic formulations. Meanwhile, the actual byproducts of many in-service multi-component pyrotechnics remain relatively unknown. Thus, it is important to characterize the gaseous and condensed-phase chemical species that arise following the deployment of pyrotechnic energetic materials to more adequately understand the potential impact that these species can present to the environment. These environmentally-objectionable chemical species can potentially arise from unreacted components of the original pyrotechnic formulation or as lower abundance species from undesirable side reactions within the combustion. Mass spectrometry (MS) enables the rapid analysis of these products with instrumentation that offers unparalleled sensitivity and techniques that provide exceptional information content. Here, we explore the utility of these measurements to qualitatively differentiate between unique pyrotechnic formulations that are designed to produce the emission of visible yellow light while eliminating the use of the perchlorate oxidizer that is currently included within the composition for the in-service yellow signal flare. Individual samples for each reacted pyrotechnic composition will be collected directly into a water-filled vessel, where these resulting aqueous samples can be introduced into the mass spectrometer via electrospray ionization. Pyrolysis-MS is then used to investigate the gaseous products that are formed from thermal decomposition of several individual components of the pyrotechnic formulation (e.g., epoxy binders, asphaltum, etc.). The identity and quantity of these chemical species will be compared against thermodynamic equilibrium calculations to assess the correlation of the actual reaction products with those predicted by theory.

**15. SUBJECT TERMS**
mass spectrometry, gas chromatography, pyrolysis, combustion products, pyrotechnics

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**Preliminary Investigation into Pyrotechnic Chemical Products via Mass Spectrometry Techniques**

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*CAPT JT Elder, USN*
*Commanding Officer*
*NSWC Crane*

# *Preliminary Investigation into Pyrotechnic Chemical Products via Mass Spectrometry Techniques*

***POC: Dr. Jonathan Dilger, jonathan.m.dilger@navy.mil***

***Prepared for: EuroPyro***

***May 5, 2015, Toulouse, France***

*Dr. Adam Razavian, SES*
*Technical Director*
*NSWC Crane*

# Outline

***Problem:*** How can we characterize the chemical byproducts that result from a pyrotechnic reaction?

***System:*** Mk 144 Yellow Signal Flare (YSF)

***Team:*** Dr. Eric Miklaszewski
Dr. Douglas Papenmeier
Matthew Neiswinger
Christina Yamamoto

***Approach:*** Pyrolysis / Gas Chromatography / Mass Spectrometry (Py/GC/MS)

***Data:*** Mk 144 standard vs. new YSF formulation
Individual ingredients from each formulation

# Yellow Signal Flare Compositions

Reformulation of the Mk 144 as an environmentally-benign composition that still meets performance requirements with a focus to eliminate perchlorate oxidizers

| | Mk144-Std | YSF-8 |
|---|---|---|
| Mg | *** | 20.10 |
| $NaNO_3$ | -- | 37.00 |
| $Na_2C_2O_4$ | *** | -- |
| $Ba(NO_3)_2$ | *** | 27.05 |
| $KClO_4$ | *** | -- |
| PVC | -- | 10.90 |
| Asphaltum | *** | -- |
| Epoxy | *** | 4.95 |

# What about the byproducts?

$$Mg + NaNO_3 + Na_2C_2O_4 + Ba(NO_3)_2 + KClO_4 + PVC + Asphaltum + Epoxy = MgO + MgCl_2 + Na + KCl + BaCl^* + BaOH^* + BaO + \textbf{gases} + \textbf{other byproducts}$$

**Products of incomplete combustion are favored within "pyrolytic pockets", areas characterized by poor micromixing of oxygen and the composition ingredients.**

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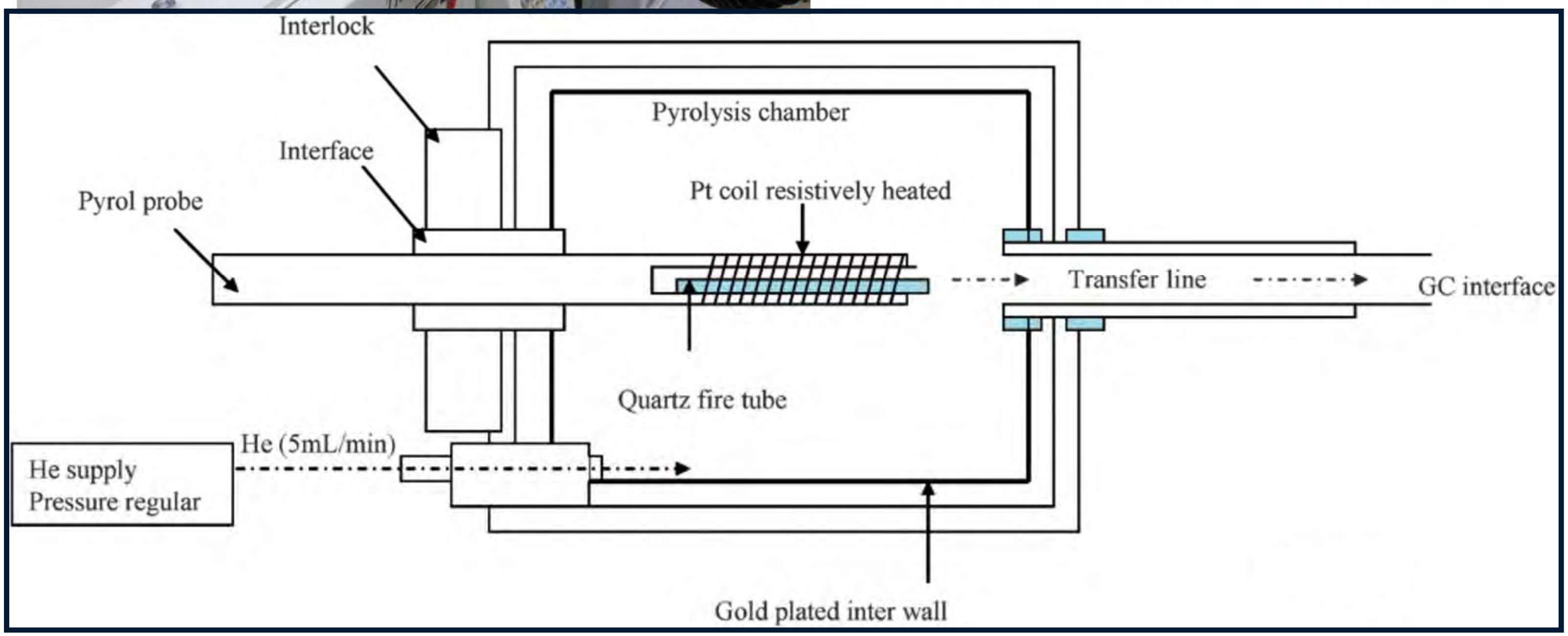
| Asphaltum | *** | -- |
| Epoxy | *** | 4.95 |

Mk 144 formulation

**DISTRIBUTION STATEMENT A.** Approved for public release; distribution is unlimited

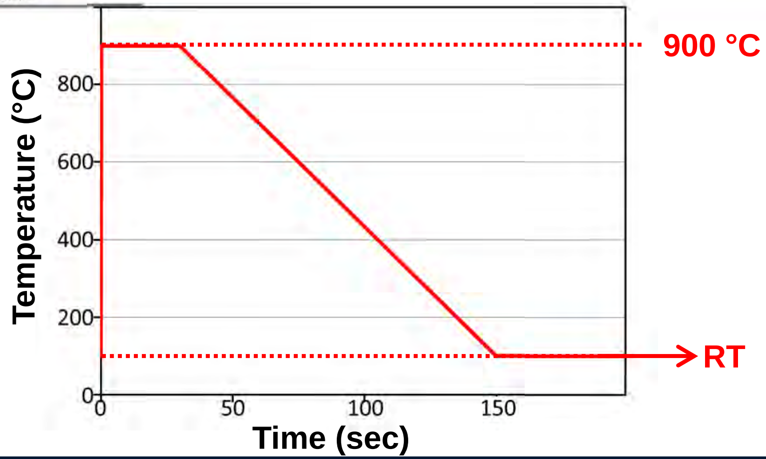
# Pyrolysis (Py)

- Pyrolysis Chamber
  - CDS 2000 pyroprobe
  - CDS 8000 preconcentrator
- Inert He buffer gas
  - GC compatible
  - *Anaerobic conditions*

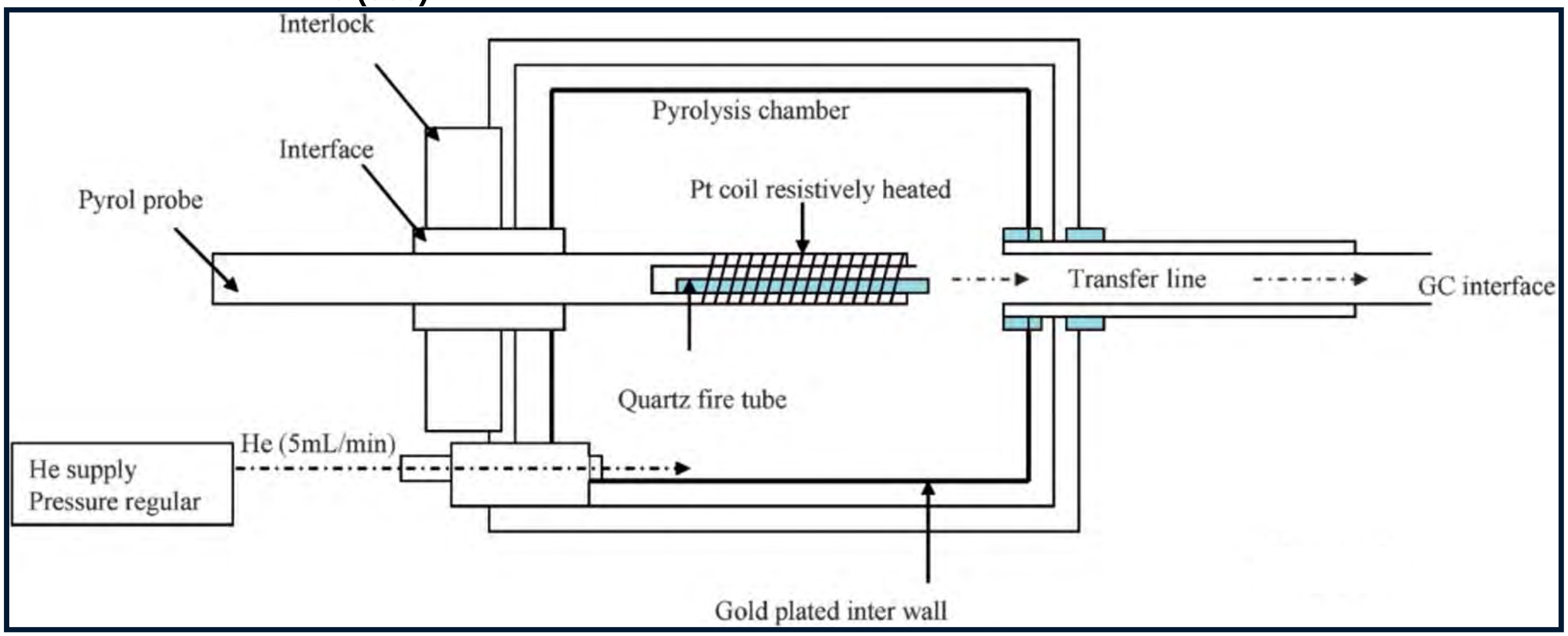



"Discrimination of bacteria using pyrolysis-gas chromotography-differential mobility spectrometry (Py-GC-DMS) and chemometrics" Goodacre *et al.*, Analyst 134 (2009), 557-563.

# Pyrolysis (Py)



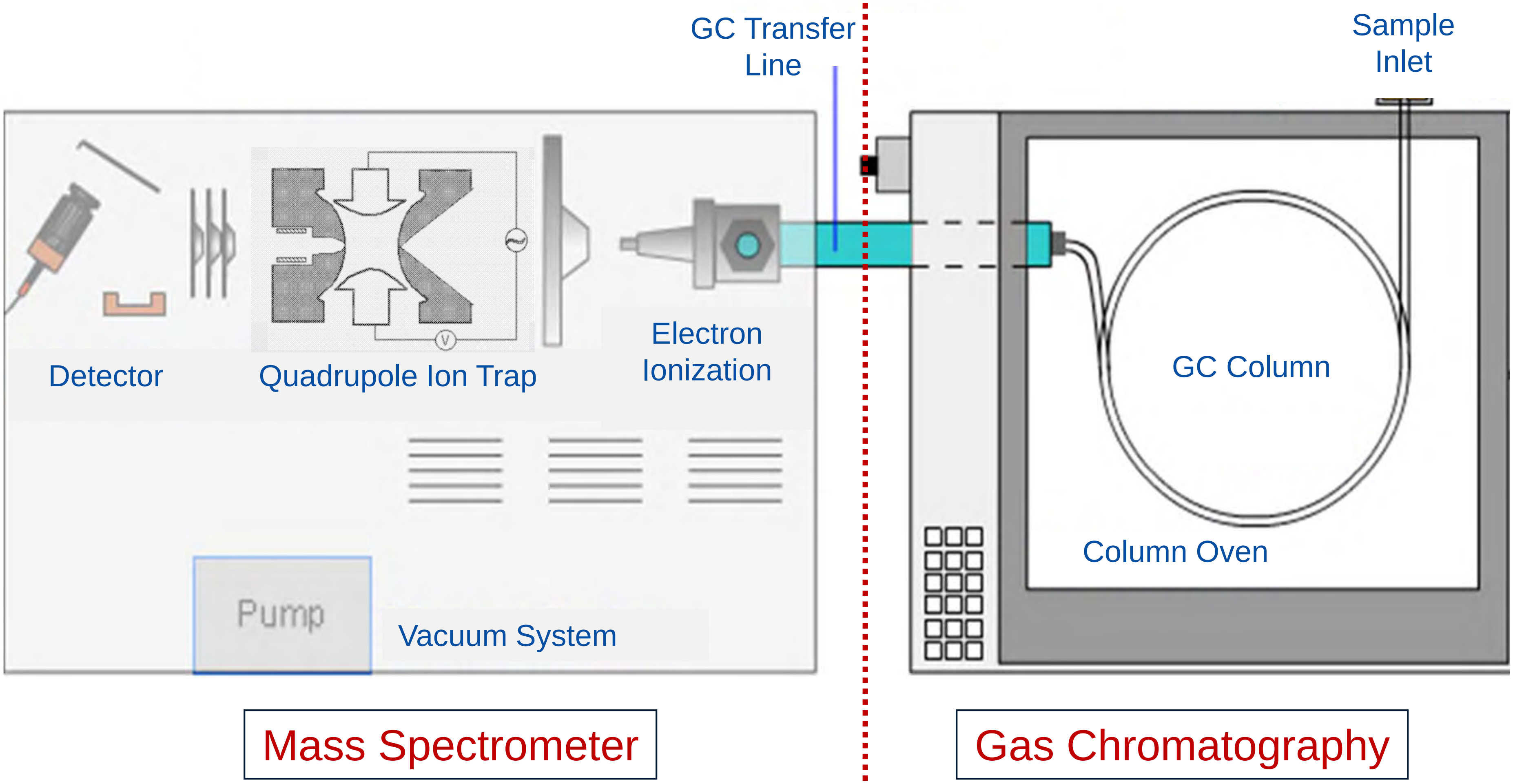

- Quartz fire tube
  - 0.2 - 2 mg of sample
  - Quartz wool to seal
- Temperature ramp
  - Pt coil: 20 °C per msec
  - 900 °C held for 30 sec




"Discrimination of bacteria using pyrolysis-gas chromotography-differential mobility spectrometry (Py-GC-DMS) and chemometrics" Goodacre *et al.*, Analyst 134 (2009), 557-563.

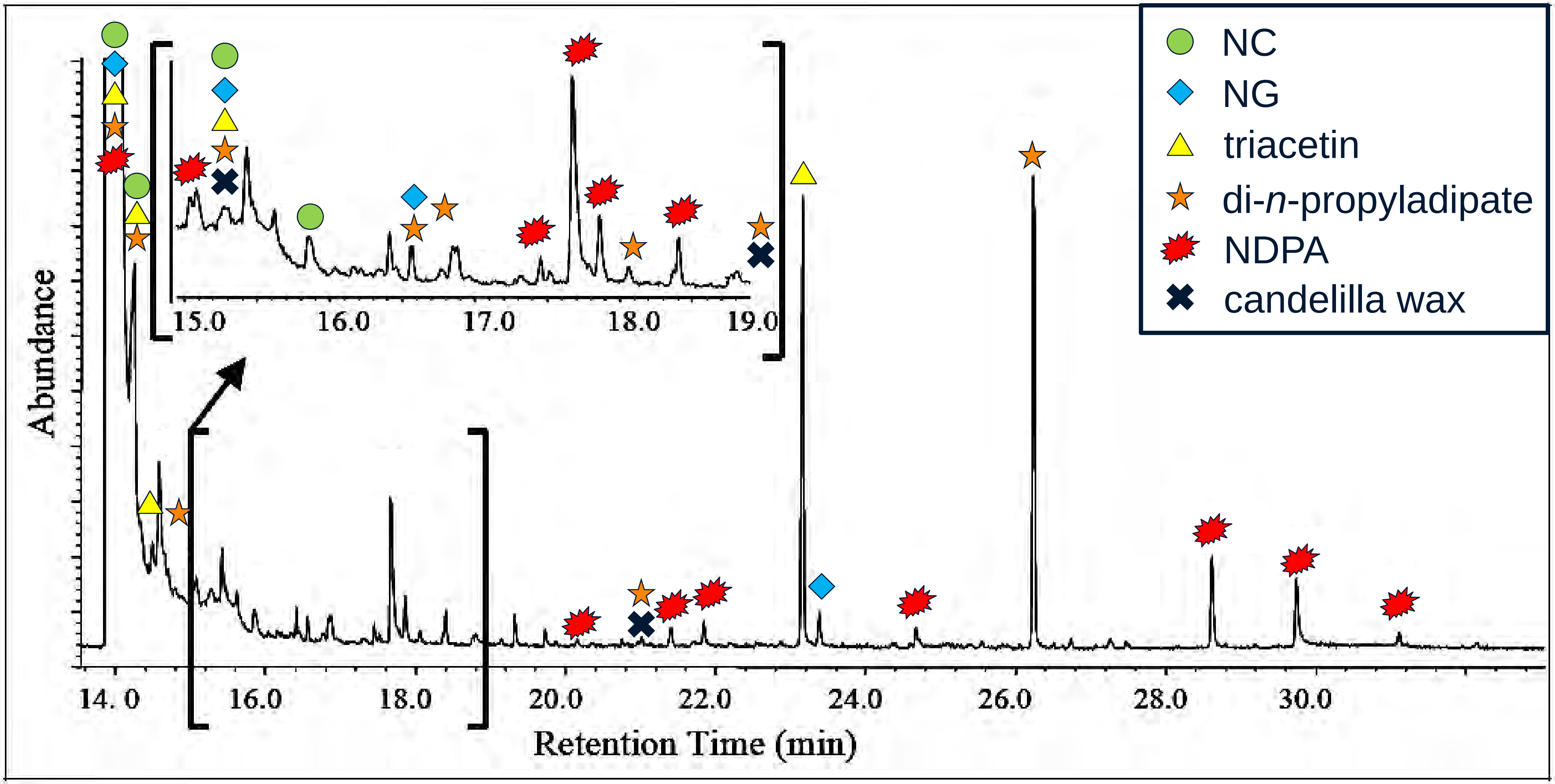
# GC/MS

Thermo Finnigan PolarisQ Ion Trap with Trace GC/MS$^n$
with a Zebron ZB-5MSi GC Column




http://www.chromacademy.com/Electron_Ionization_for_GC-MS_Essential_Guide.html

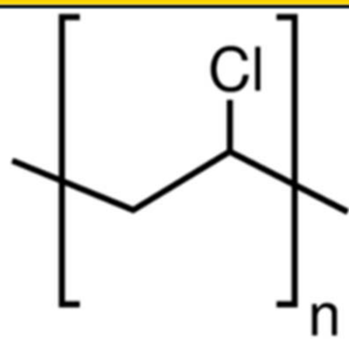
# Pyrolytic Chromatogram



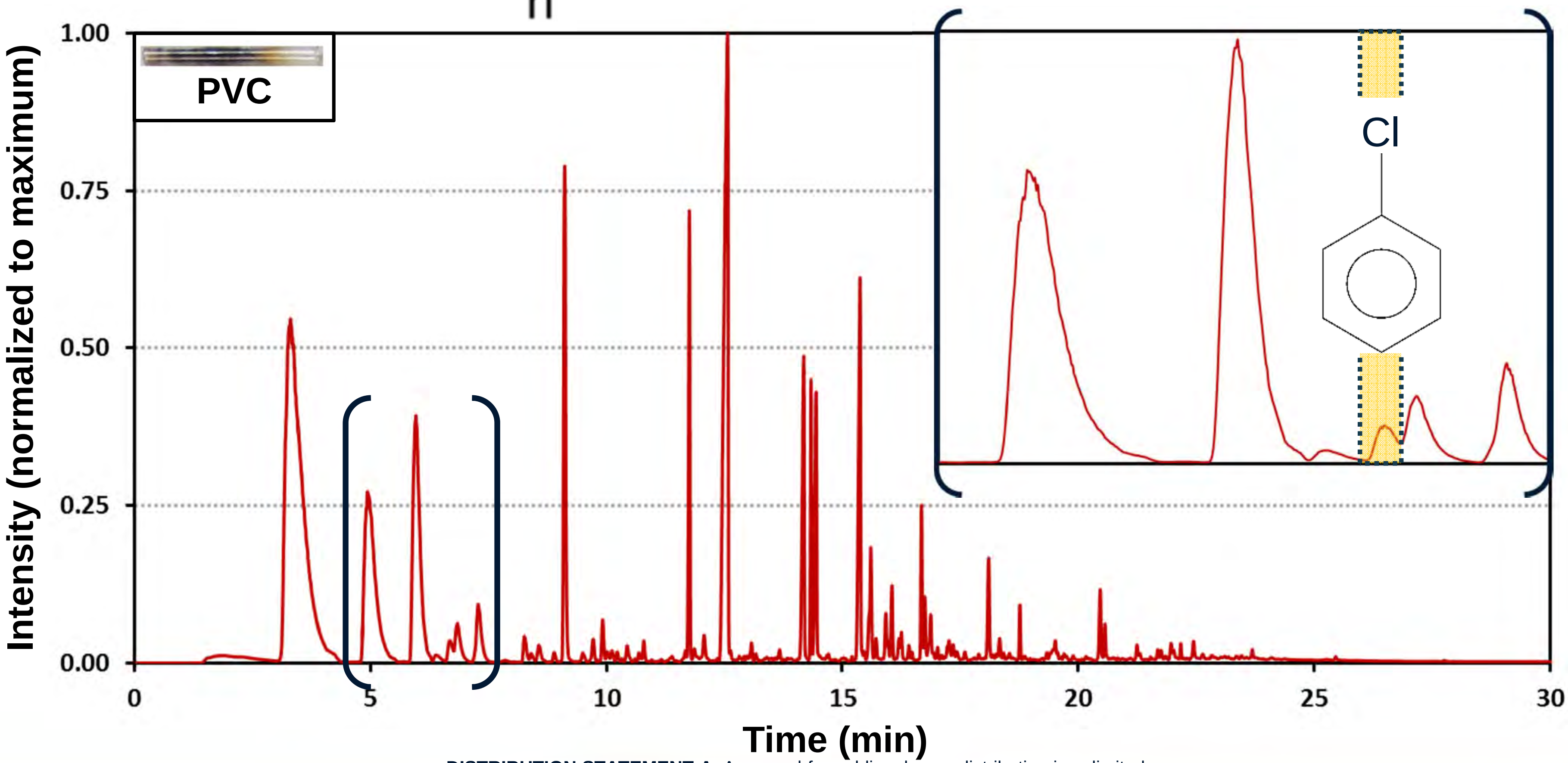

**High molecular weight pyrogram for the AA2 double-base propellant composition.**


"Use of Pyrolysis GC/MS for Predicting Emission Byproducts from the Incineration of Double-Base Propellant"
Cropek *et al.*, Environ. Sci. Technol. 36 (2002), 4346-4351.

# Py/GC/MS: PVC




- Linear, strong polymeric chains
- Chlorines on alternating carbon centers
- Random stereochemistry of the chloride centers



# Py/GC/MS: PVC

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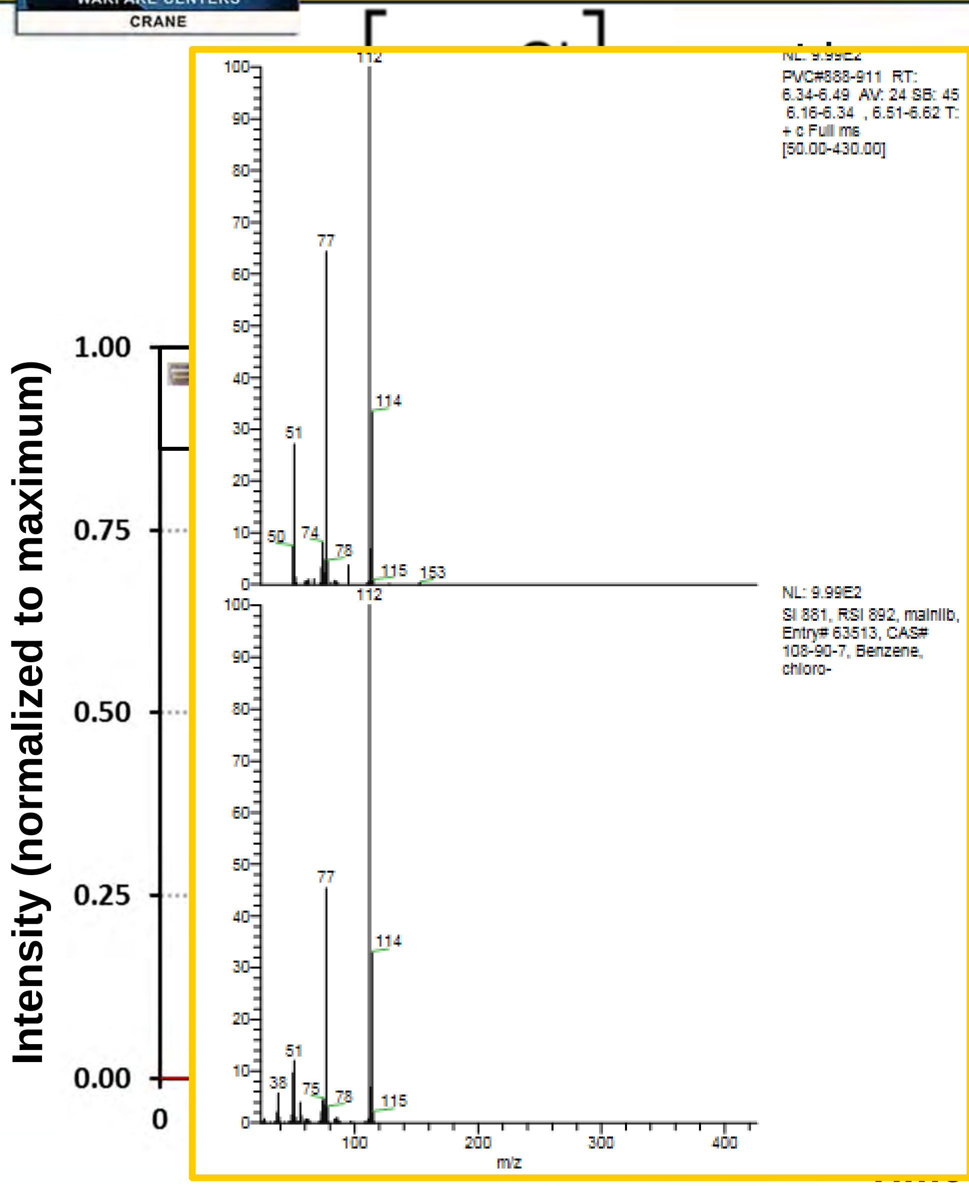
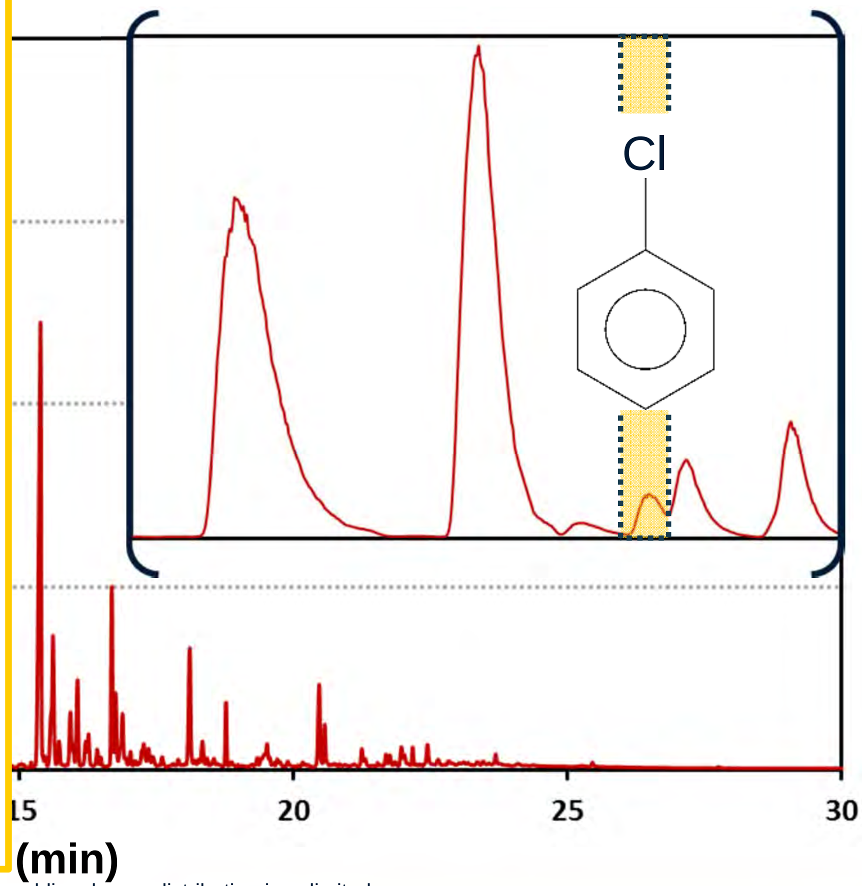
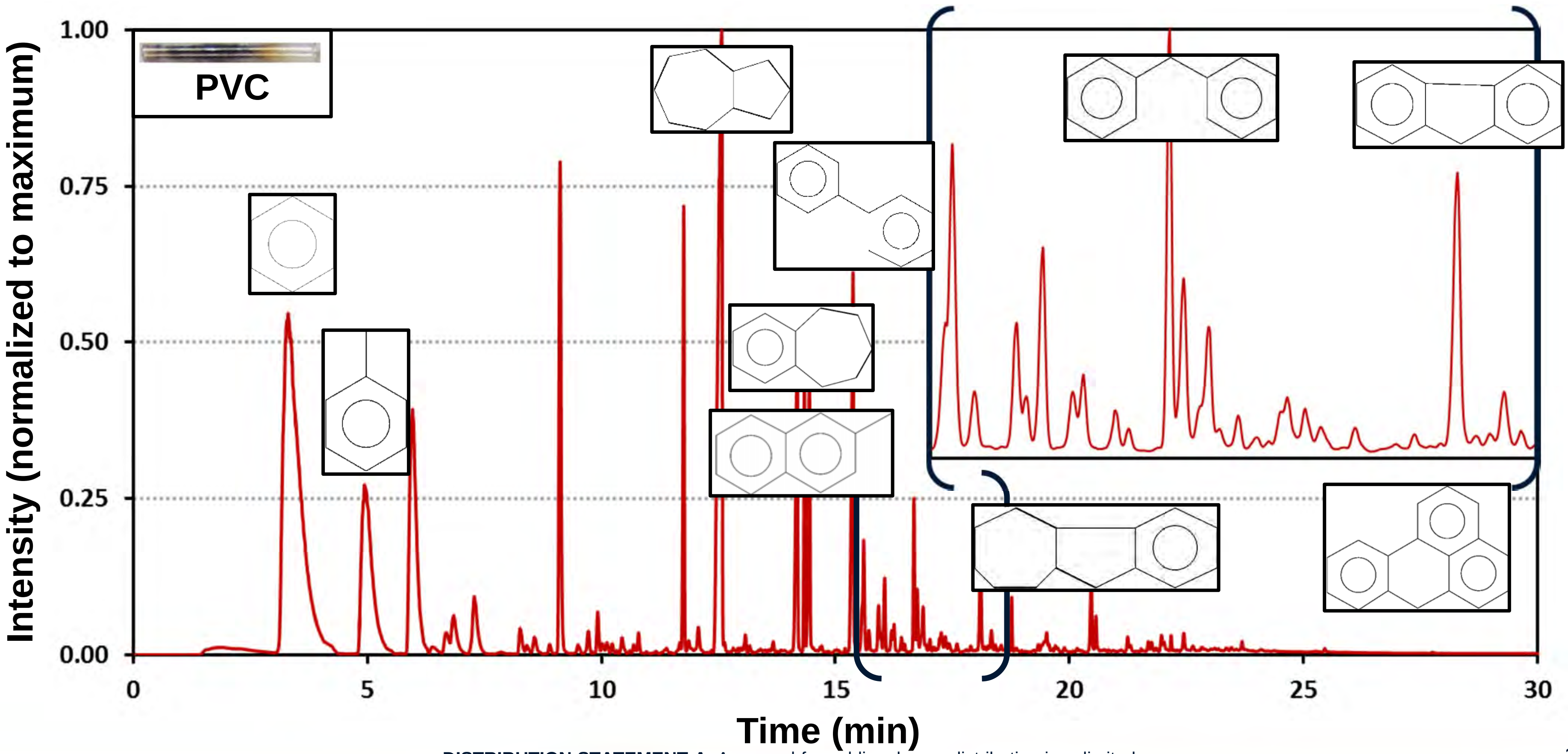


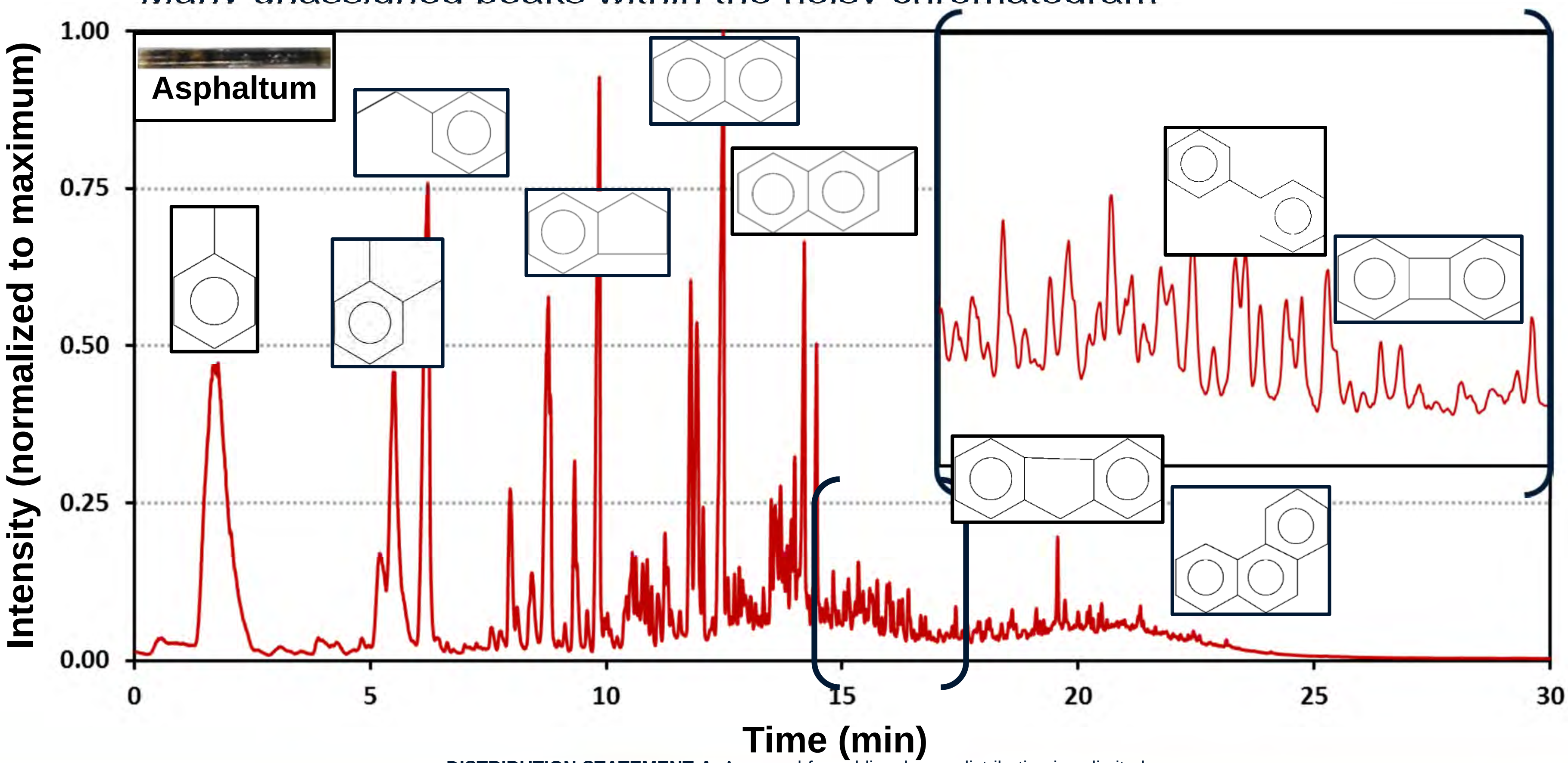
# Py/GC/MS: PVC

- Pyrolysis of PVC exclusively yield cyclic hydrocarbons
  - 24.3% benzyl derivatives and 75.6% polycyclic aromatic hydrocarbons (PAH)
  - 1% of all identified species are chlorinated

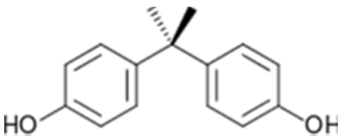


# Py/GC/MS: Asphaltum

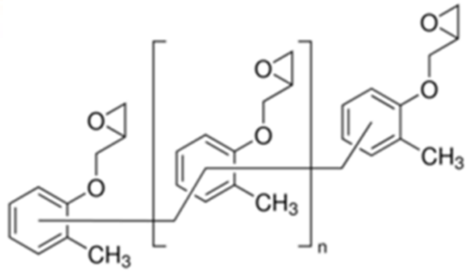
- Pyrolysis of Asphaltum also exclusively yield cyclic hydrocarbons
  - Powdered bitumen-impregnated rock
  - Highly complex; difficult to obtain confident MS assignments
  - Many unassigned peaks within the noisy chromatogram



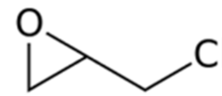
# Py/GC/MS: Epon/Versamid



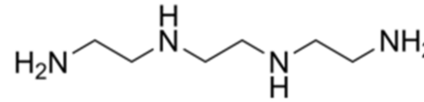
bisphenol A



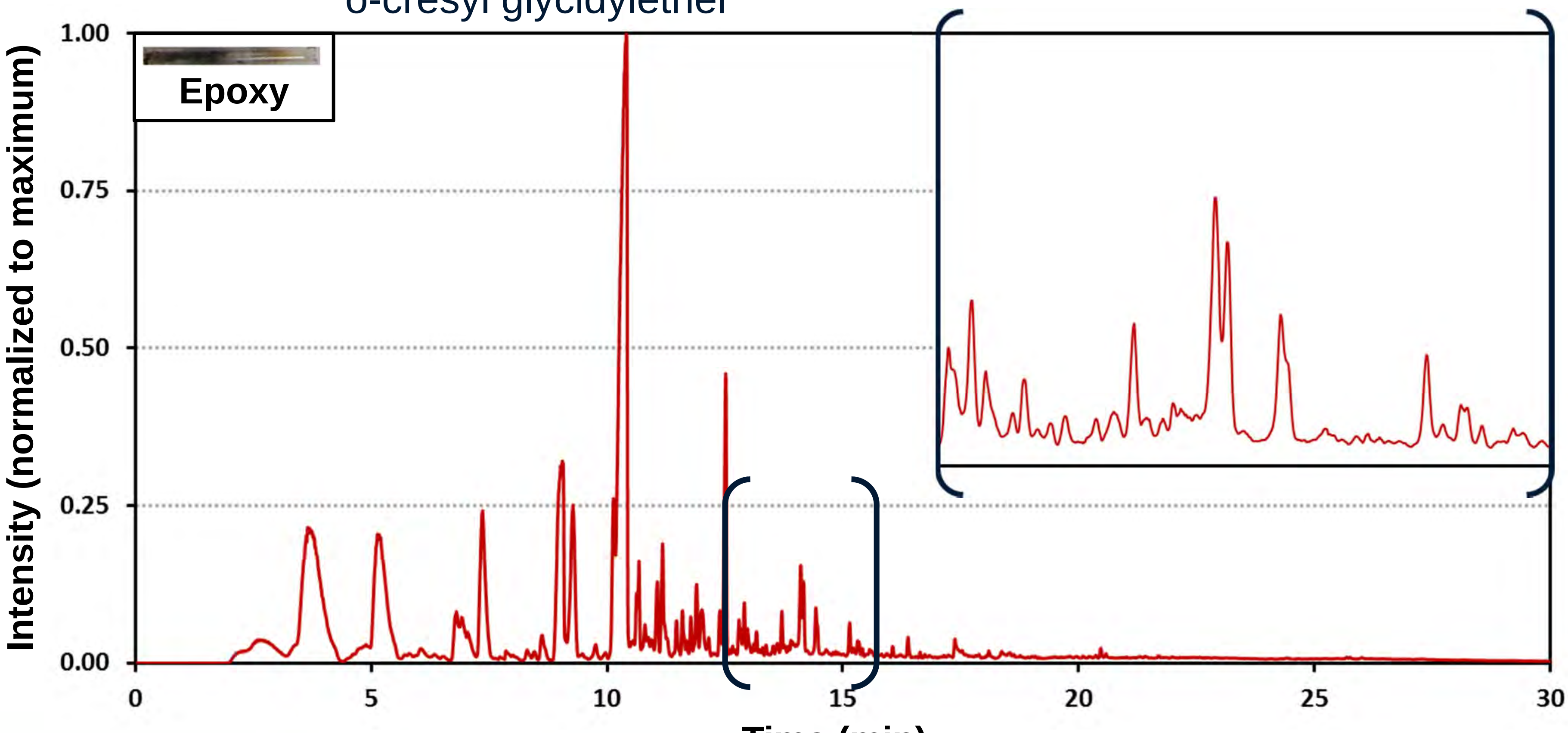
o-cresyl glycidylether



epichlorohydrin

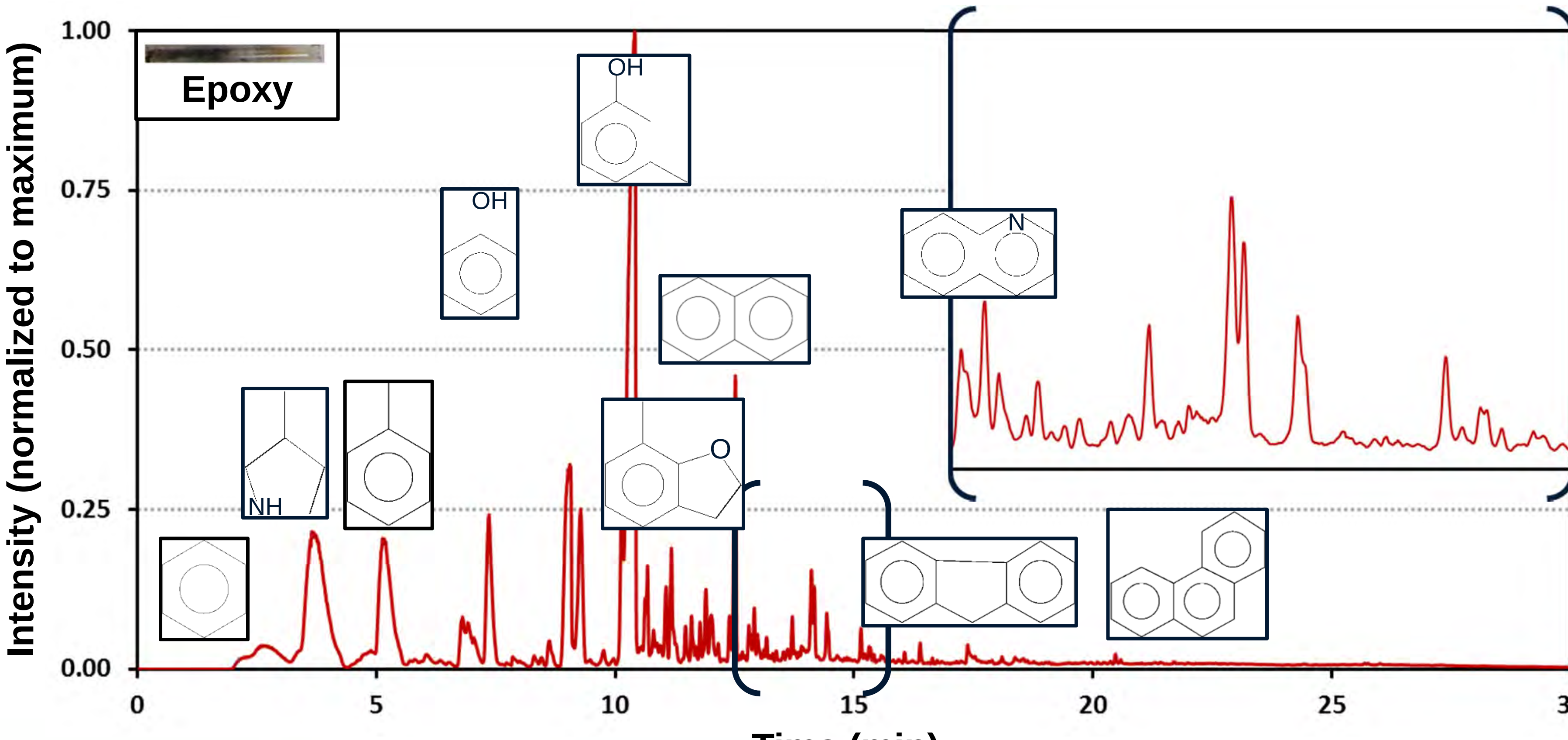


triethylenetetramine

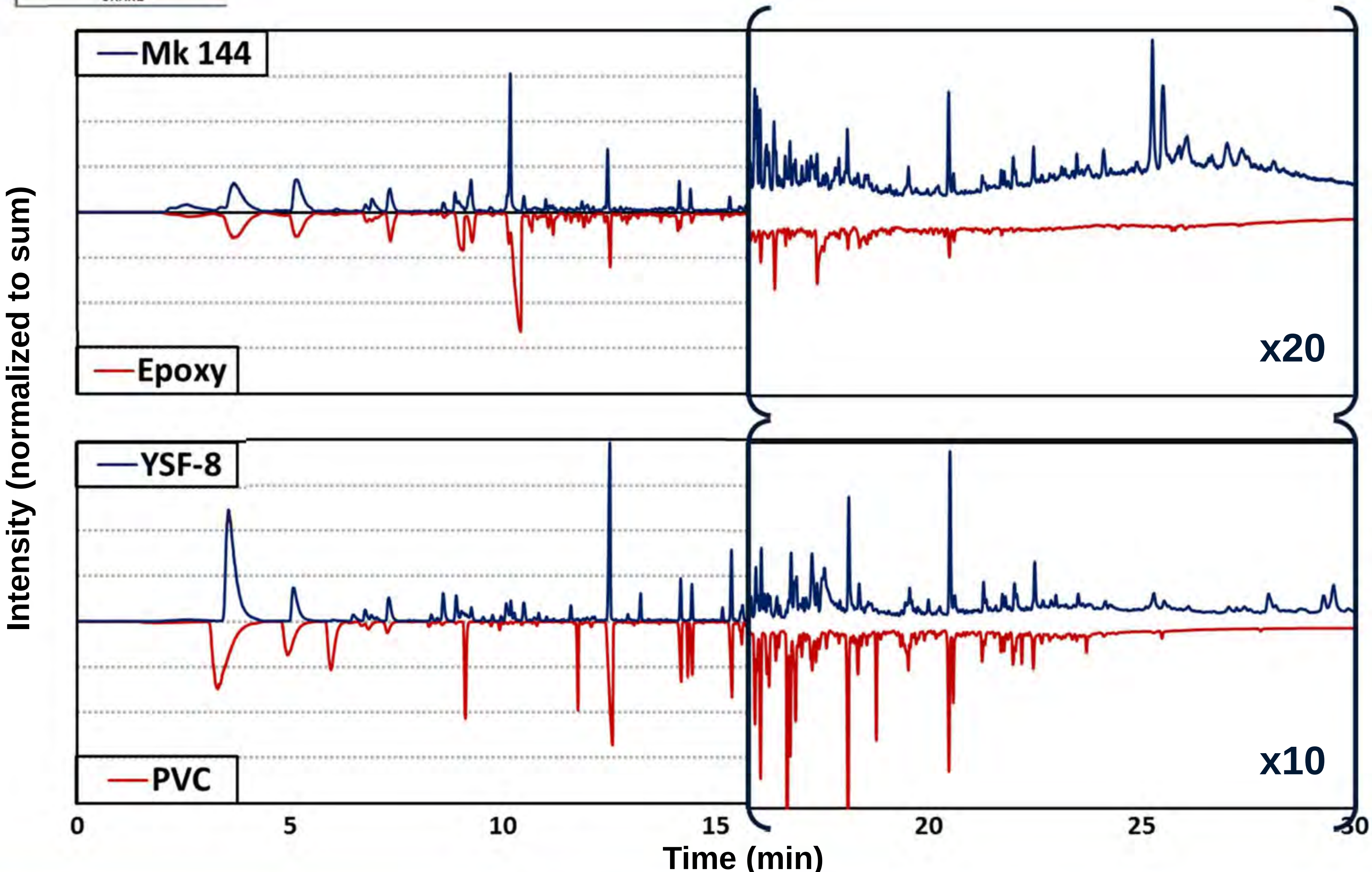


# Py/GC/MS: Epon/Versamid

- Pyrolysis of Epon/Versamid yields PAHs, phenols, pyridines, & pyrroles
  - 67.8% benzyl derivatives and 31.2% polycyclic aromatic hydrocarbons (PAH)
  - 42.3% hydrocarbons, 53.5% phenols, 4.7% nitrogen-containing

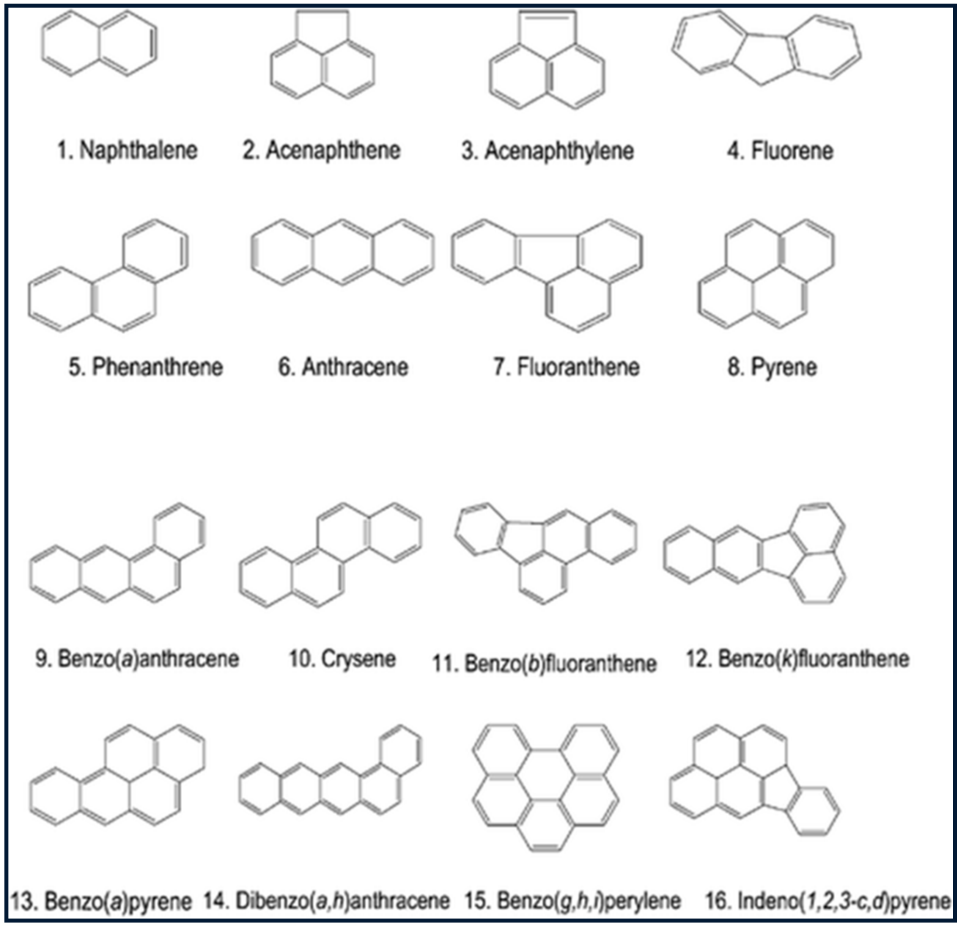


# Py/GC/MS: Pyro Compositions



# PAHs: Why the concern?

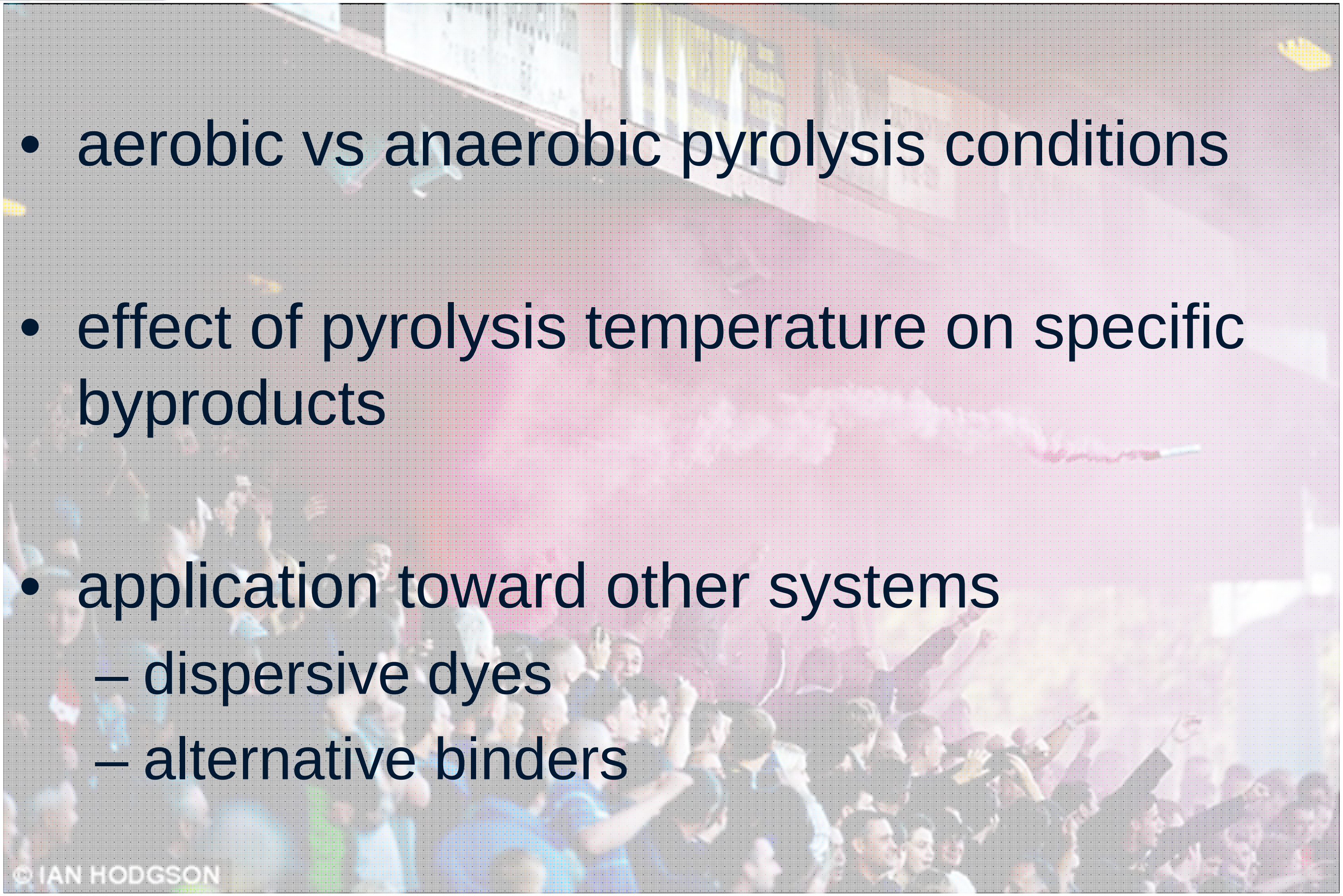
The United States Environmental Protection Agency (EPA) has designated 32 PAHs as Priority Pollutants




- Benzopyrene – first discovered chemical carcinogen
- Known for their carcinogenic, mutagenic, and tartogenic properties
- Targeted by the EPA for measurement within environmental samples

"Determination of EPA's priority pollutant polycyclic aromatic hydrocarbons in drinking waters by solid phase extraction-HPLC" Bruzzoniti *et al.*, Anal. Methods 2 (2010), 739-745.

# Future Directions




- aerobic vs anaerobic pyrolysis conditions
- effect of pyrolysis temperature on specific byproducts
- application toward other systems
  - dispersive dyes
  - alternative binders

http://www.dailymail.co.uk/sport/football/article-2510036/Ash-Wednesday--Premier-League-launch-campaign-combat-use-flares-smoke-bombs.html

# Backup Slides

# Py/GC/MS: Pyro Compositions

- Pyrolysis of the PVC-containing composition produced ~2x the volatile organic molecules
  - high similarity in chromatographic elutions with relative intensity differences
  - polyaromatic hydrocarbons (PAHs)